



U.S. Department of Energy
Office of Civilian Radioactive Waste Management



Flowthrough Dissolution of CSNF Under Oxidizing Conditions

Presented to:
DOE/CEA Technical Meeting

Presented by:
Brady Hanson
Geologic Disposal Support Project, Manager
Pacific Northwest National Laboratory

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ROUND ROBIN RESULTS - UO₂

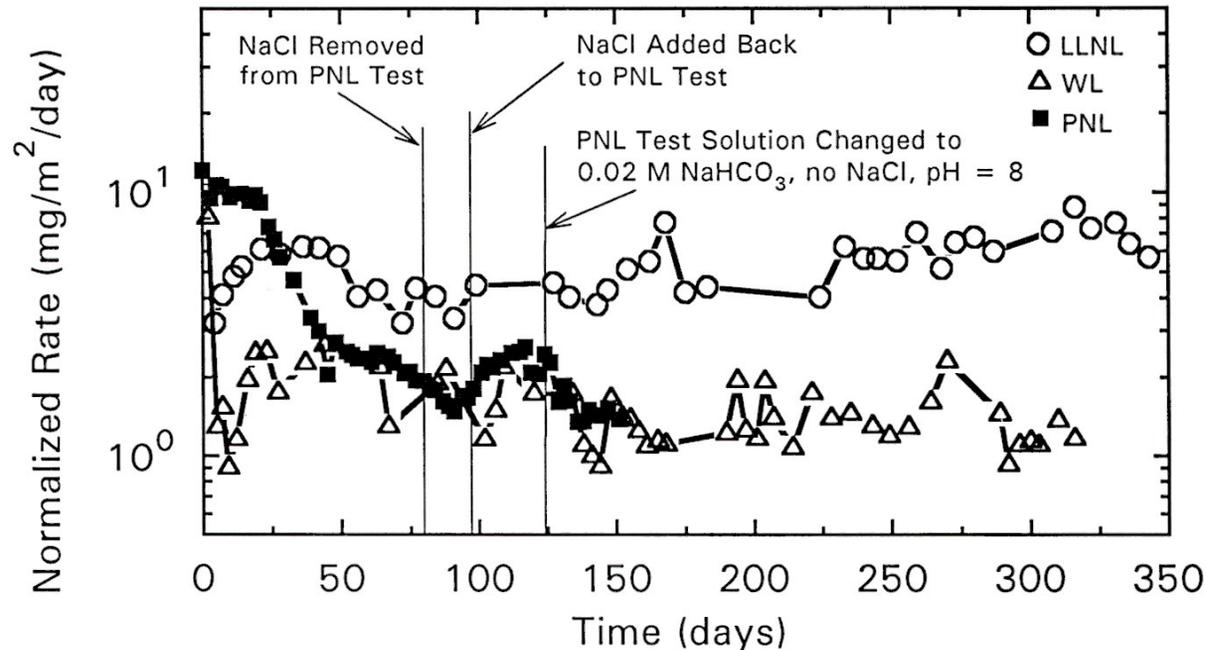
- PNNL, LLNL, Whiteshell

- Differ by a factor of 2 – 5

- Shape of the curves are quite different

- Frit size/material

- PNNL 2 μm SS
- WL 5 μm SS
- LLNL ?? Teflon
- (Röllin et. al. Teflon vs. SS)



UO₂ dissolution rate. Test solutions were 0.01 M NaHCO₃, 0.1 M NaCl, pH = 9, 25°C, except as noted.

Gray et al., Proc. International High Level Waste Management Conference, 1994

PNNL sample subjected to 3 previous water chemistries prior to the data reported here

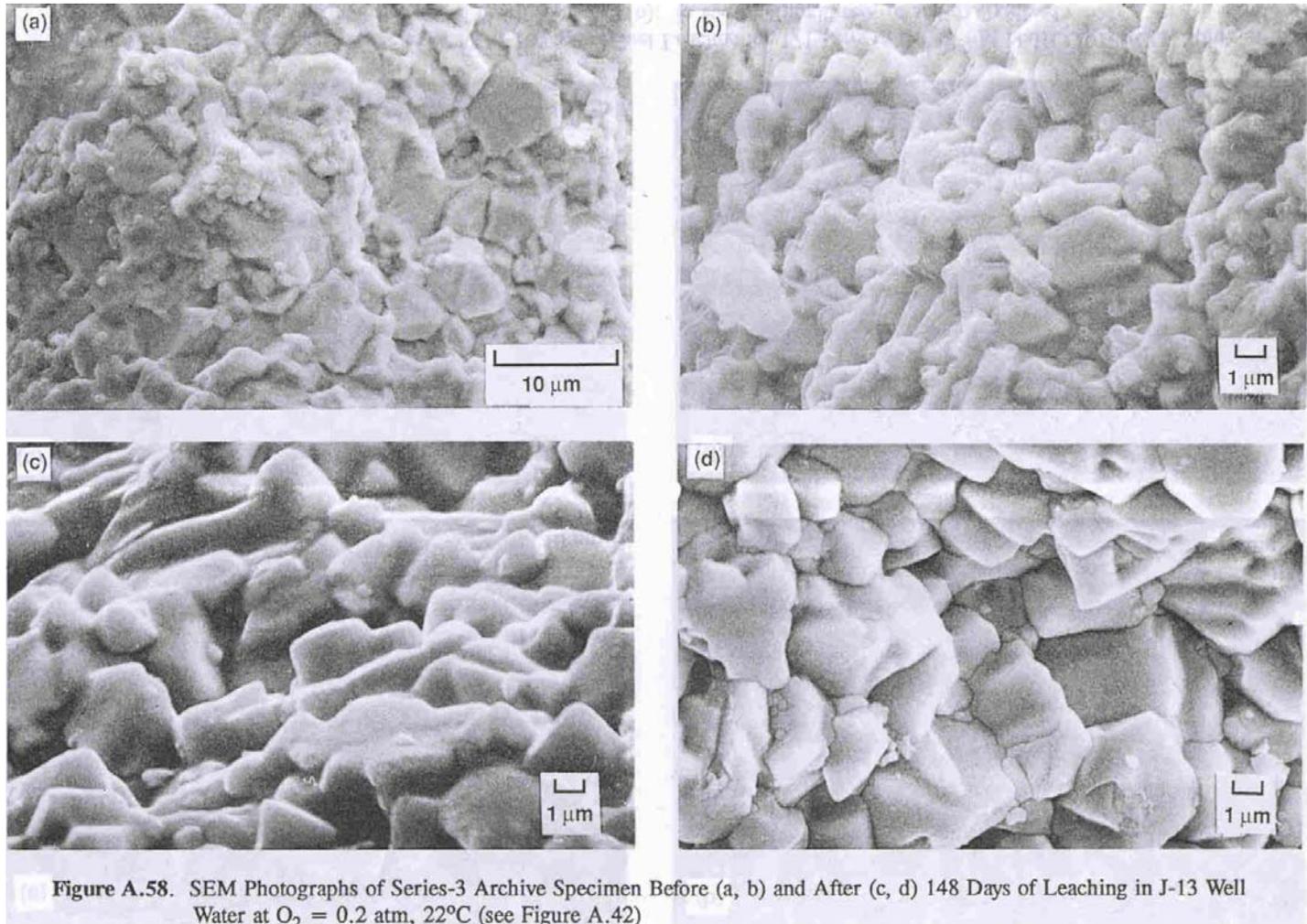


SURFACE CHEMISTRY EFFECT

Alteration layer from Wilson test stayed “intact” even after 148 days in a flow-through test.

Disappeared after another ~130 days

∴ Reuse of samples is not recommended

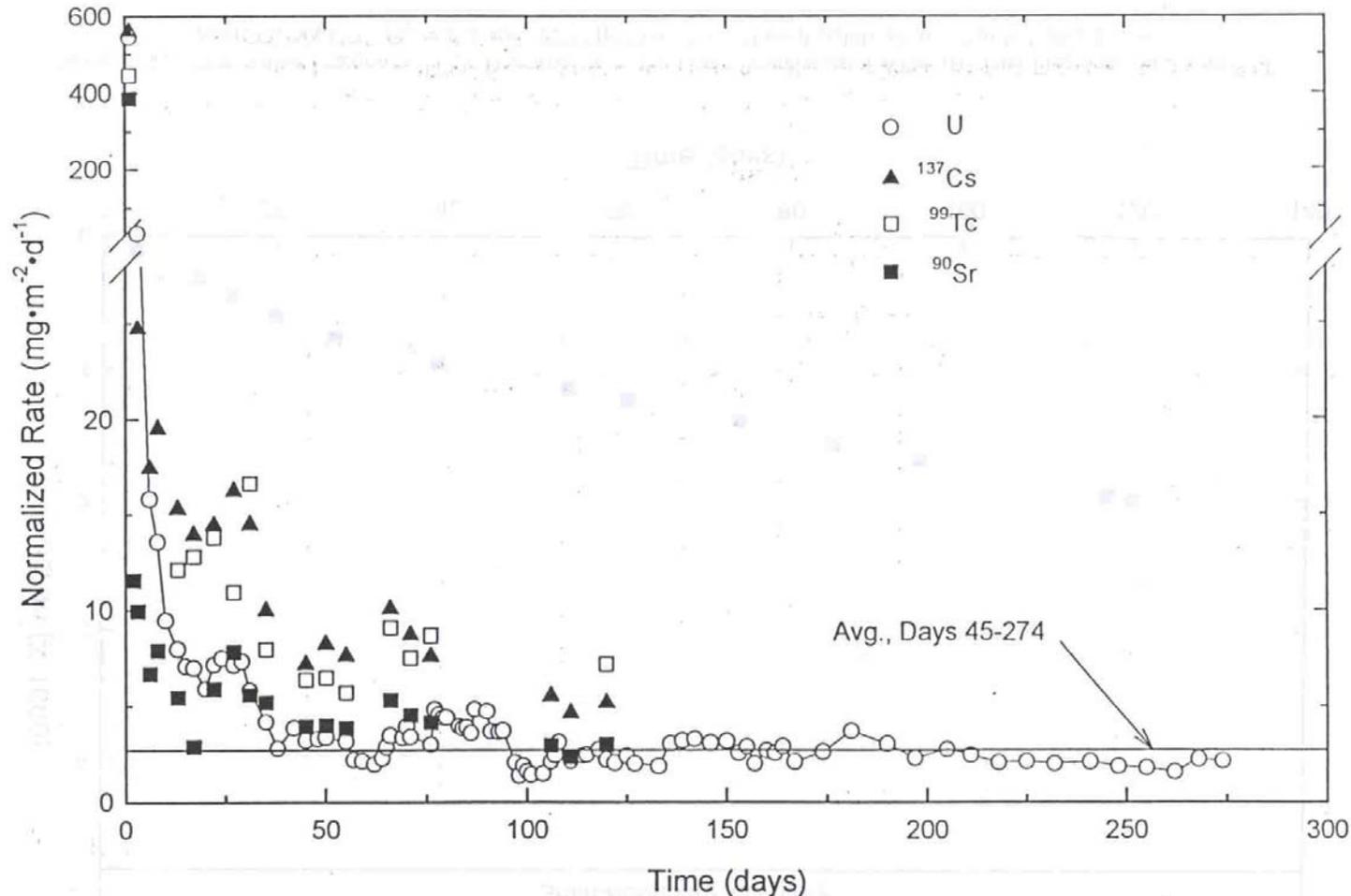


Gray and Wilson, PNL-10540, December 1995



ALTERATION PHASE EFFECT ON DISSOLUTION RATE

No significant change in rate observed in the Wilson \Rightarrow SPFT test, but does it make sense?



Tait & Luht, 1997: “When the leachant was switched to the standard carbonate solution, the dissolution rate increased by over an order of magnitude, but was highly erratic, suggesting that adsorbed silicate or secondary phases may continue to affect the dissolution rate.”



FRIT SIZE EFFECT

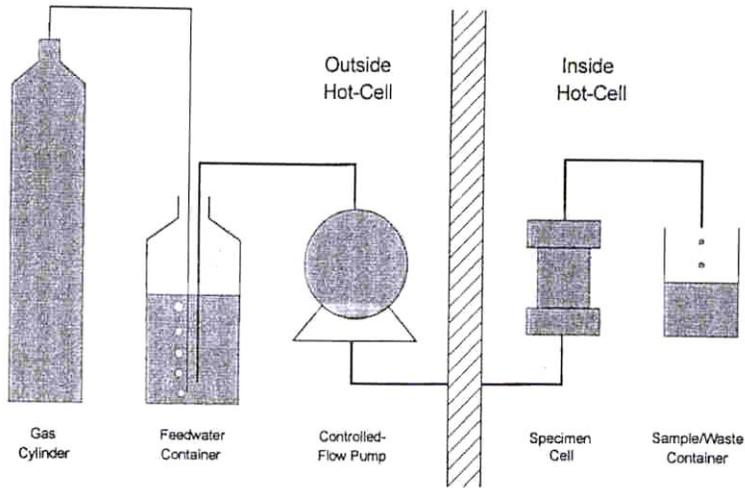


Figure 1. PNNL Flow Test Set-Up

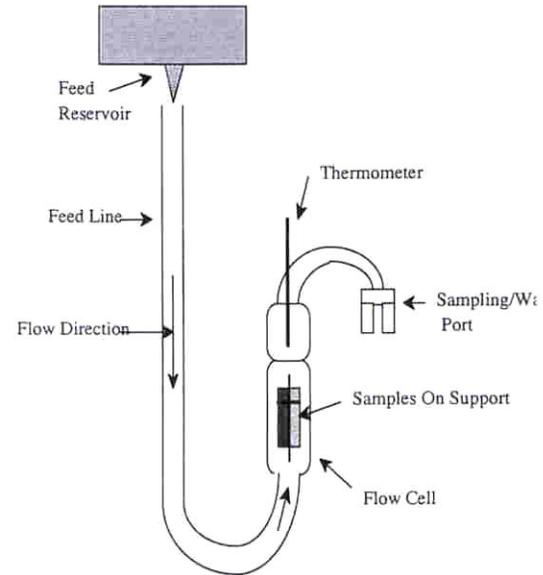


Figure 2. SRS Flow Test Cell

Wiersma & Mickalonis, WSRC-TR-98-00290 (U), August 1998

PNNL used 2 μm stainless steel frit; SRS had no frits

SRS dissolution rate was 10 \times that of PNNL



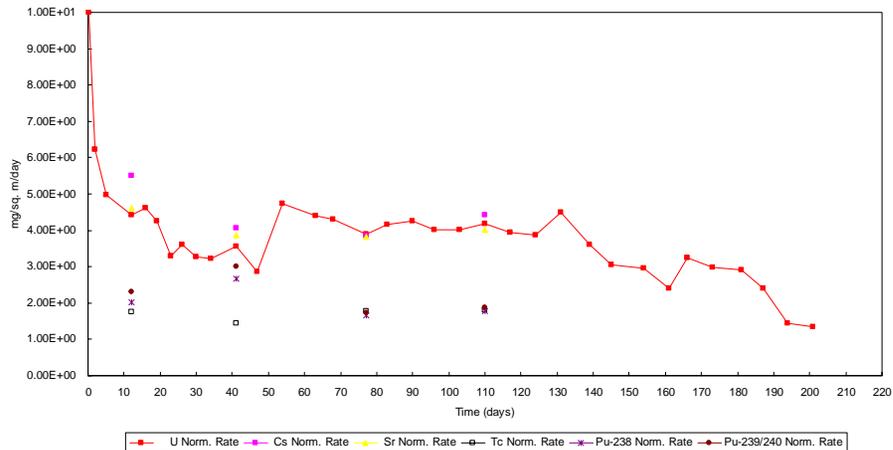
REANALYSIS OF SNF LEACHATES

- **CSNF and DOE (MOX, metallic) fuels tested**
 - Frit sizes 0.5 μm – 5 μm
- **Leachates acidified to pH<2 (typically <1)**
- **Total U concentration using Kinetic Phosphorescence Analysis (KPA)**
- **Archived samples reanalyzed (1 month-1.5 years)**
- **[U] increased in every case, sometimes as much as a factor of 20+, average of 20%**
- **Polynuclear chains, colloids, complexes (carbonates), U(IV) or U(V)**

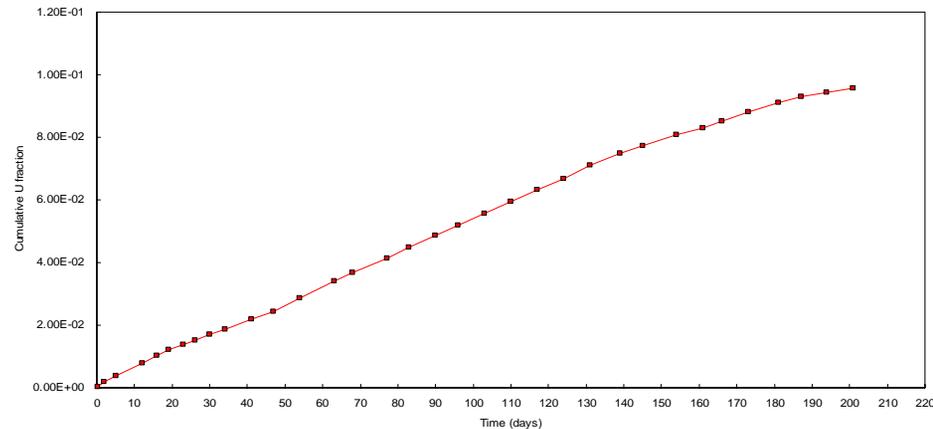


EFFECT OF DISSOLVED OXYGEN, TEMPERATURE AND RADIOLYSIS?

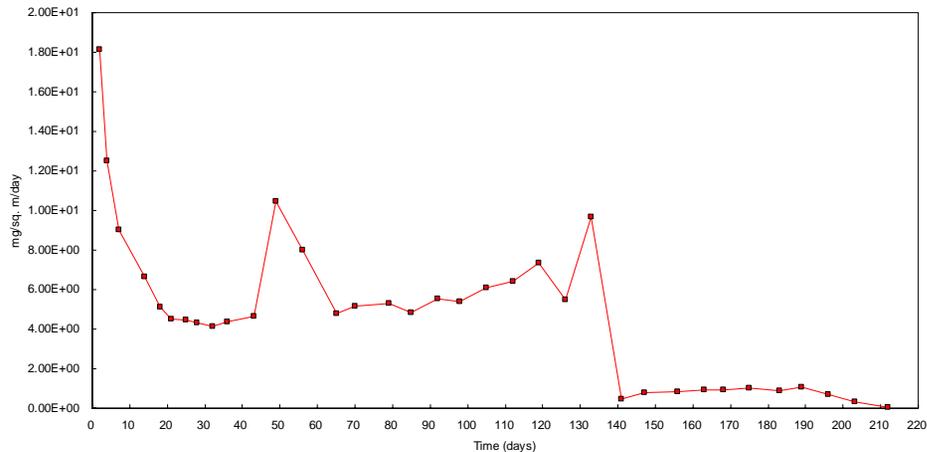
URANIUM DISSOLUTION RATE
Y9C-4L (20 mM, pH = 8)



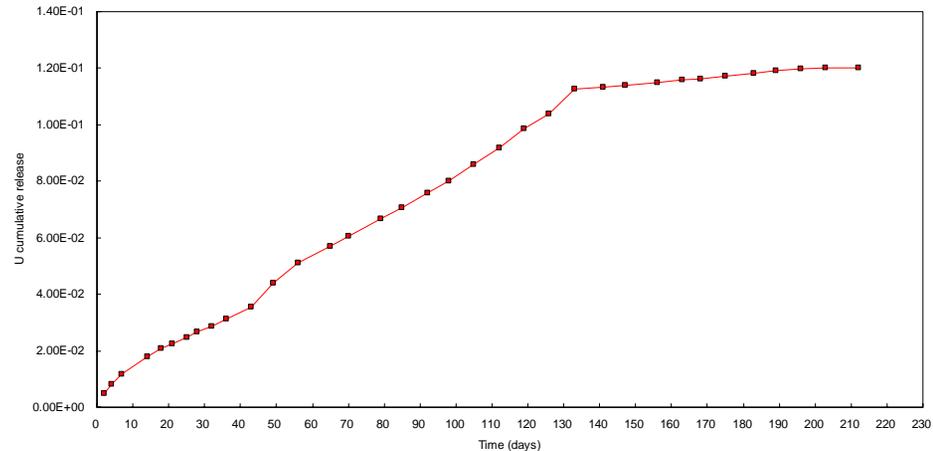
URANIUM CUMULATIVE RELEASE
Y9C-4L (20 mM, pH = 8)



URANIUM DISSOLUTION RATE
Y9C-4H (20 mM, pH = 8)



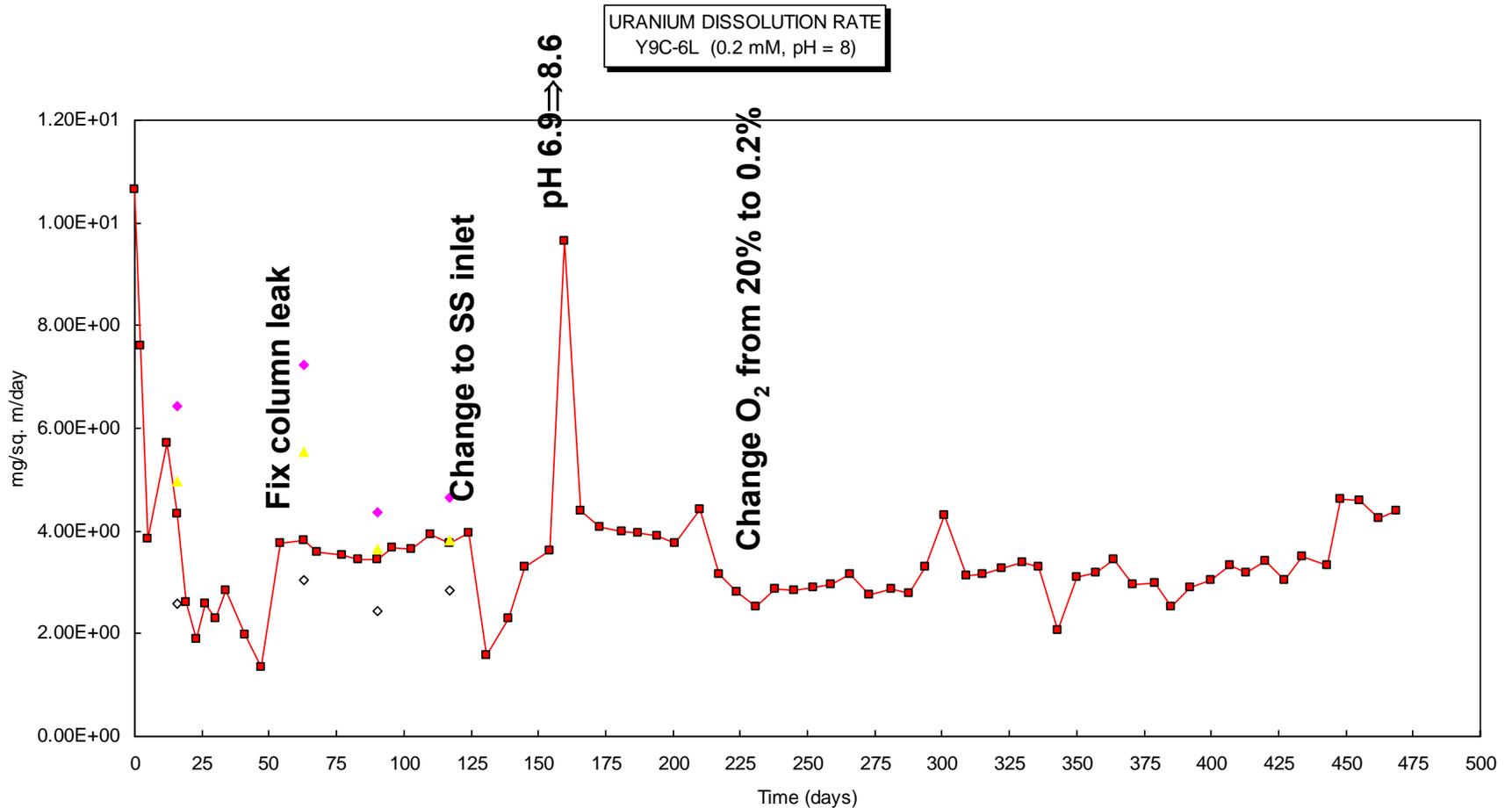
URANIUM CUMULATIVE RELEASE
Y9C-4H (20 mM, pH = 8)



H₂O₂ not stable at high temperatures, other recombination?



EFFECT OF OTHER VARIABLES



pH range: 6.78-8.65
Average: 7.63

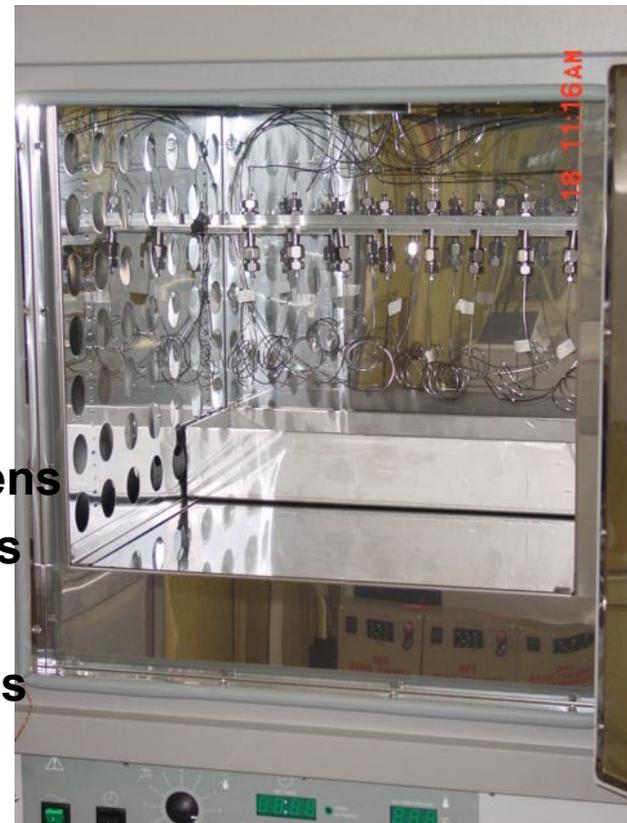
—■— U Norm. Rate —◆— Cs Norm. Rate —▲— Sr Norm. Rate —◇— Tc Norm. Rate



IMPROVEMENTS TO SPFT TESTS

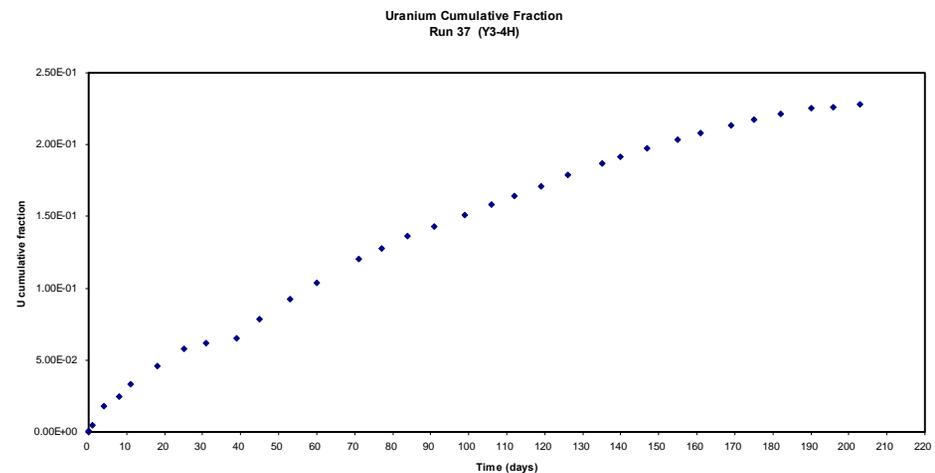
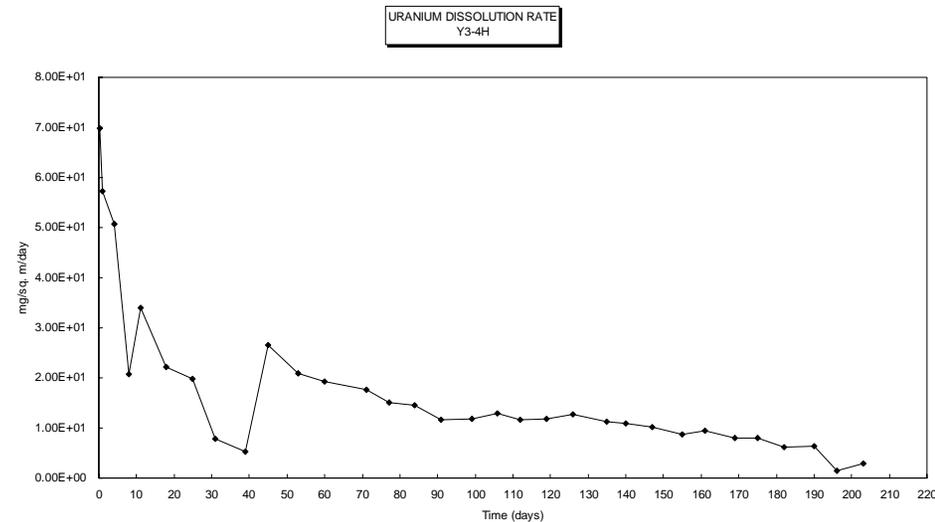


- **Leachant pre-equilibration (pre-heat, sparge)**
- **Continuous**
 - Mixing
 - Sparging
 - pH
 - Dissolved O₂
- **High precision ovens**
- **High quality pumps**
- **All SS piping**
- **Consistent analysis time for leachates**
- **Uniform frit size**
- **Fresh samples**
- **Sample characterization**

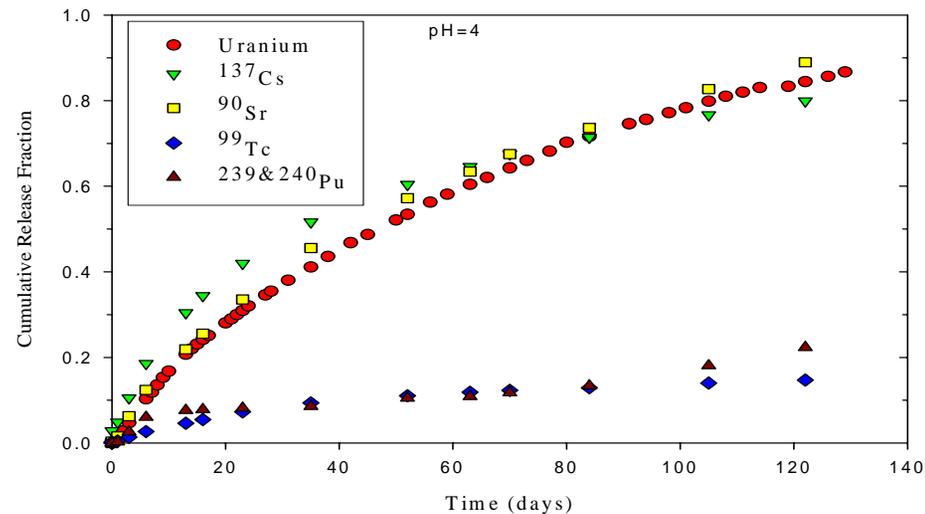
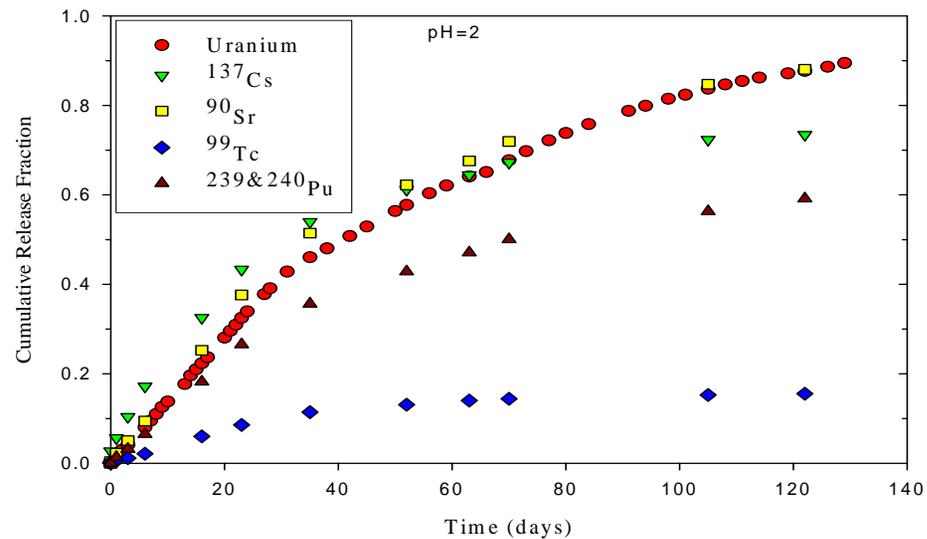
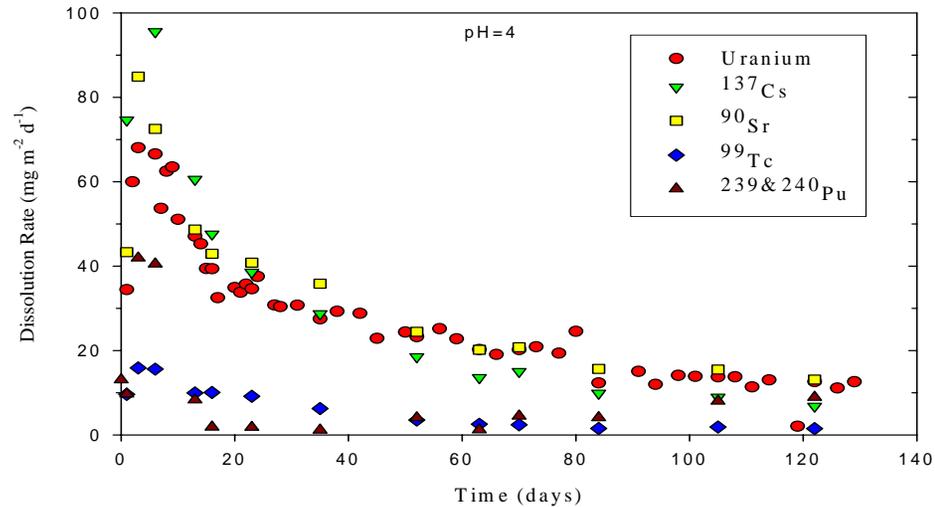
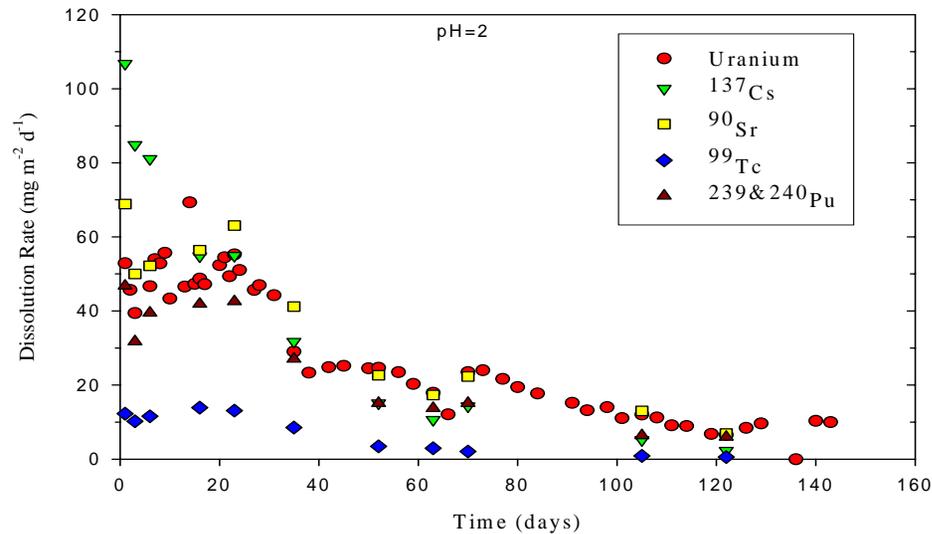


DECREASING NORMALIZED RATE

- Under most conditions cumulative release was only a few percent
- Only 2 cases under alkaline conditions where extent of reaction > 20%
- Decreasing normalized rate is typical, but if SA was increasing the rate should be increasing
 - Only data on post- vs. pre-dissolution SA show significant (factor of 50-350) increase (Hanson & Stout, MRS 2004)
 - ◆ Wormy texture
 - Loss of high-energy features
- Not a uranium alteration phase effect
 - ↓
 - Fuel chemistry**



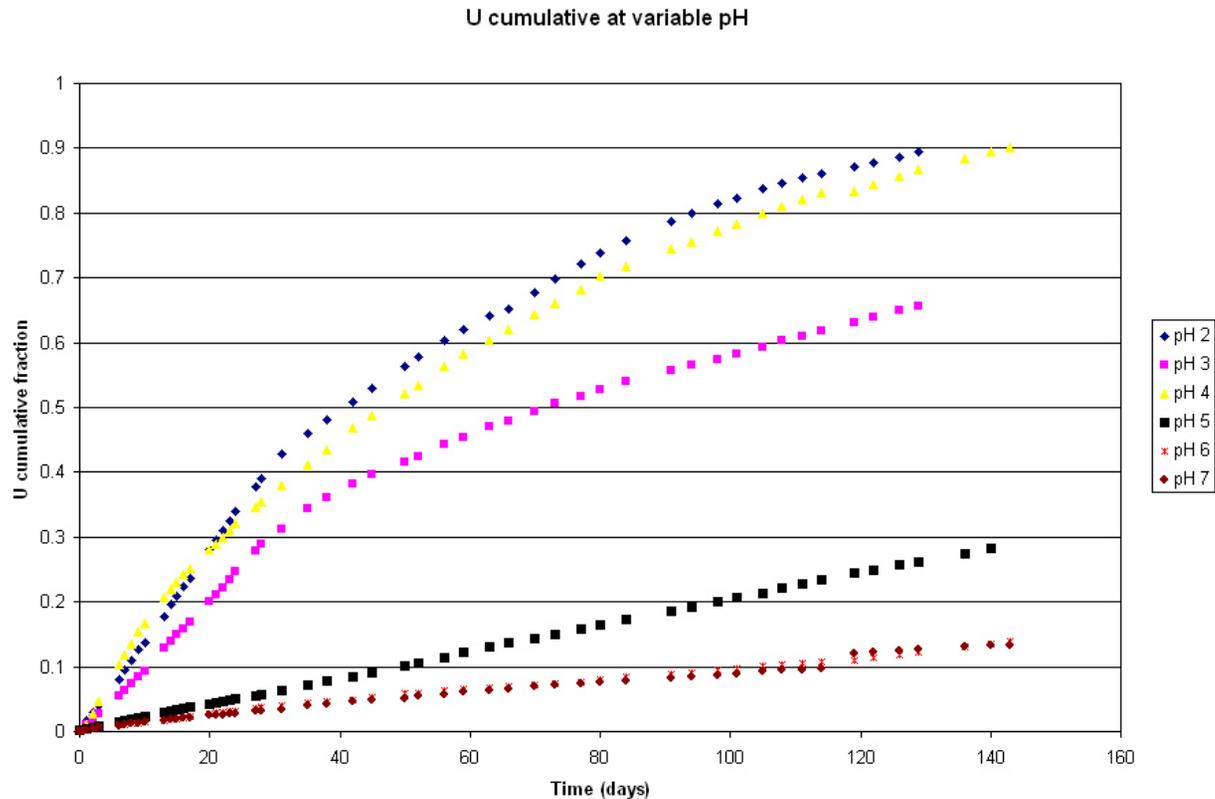
LOW pH SPFT RESULTS



Hanson et al. MRS 2004



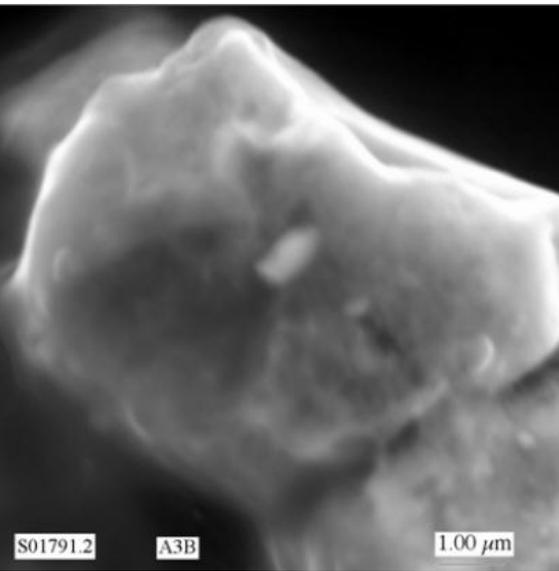
CUMULATIVE RELEASE LOW pH SPFT



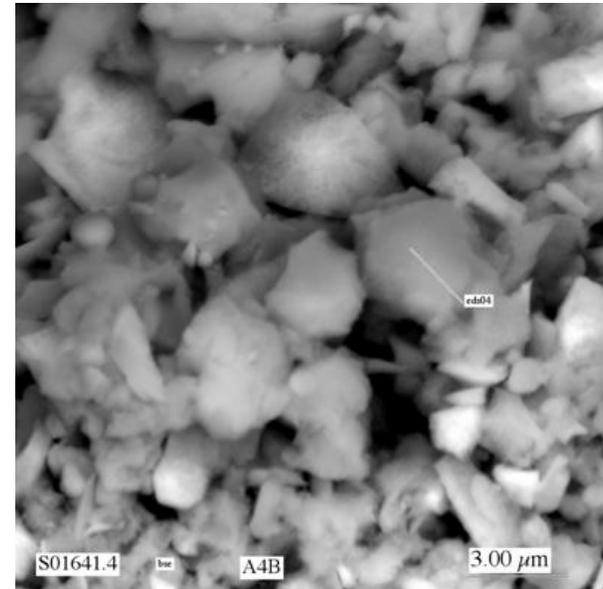
- Flowthrough tests using ATM-106 (~50 MWd/kg, 23 year decay, 18% fission gas release) powders (10-25 μm) in de-ionized water with HNO_3 added, sparged with CO_2 -free air, at 25°C. Not washed, pre-equilibrated water, flow up.



SOLIDS CHARACTERIZATION

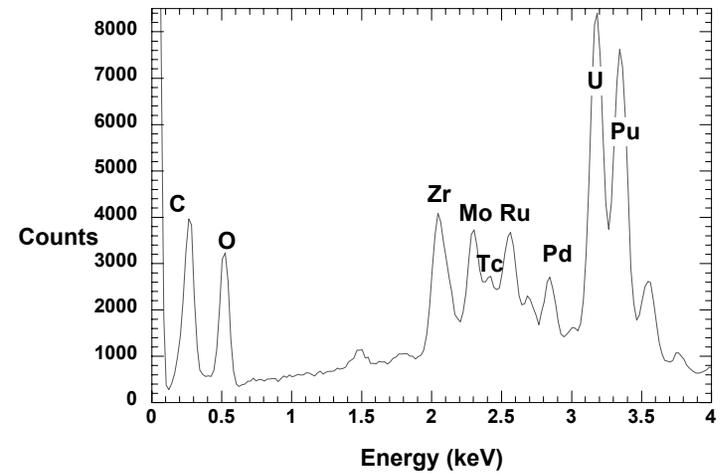
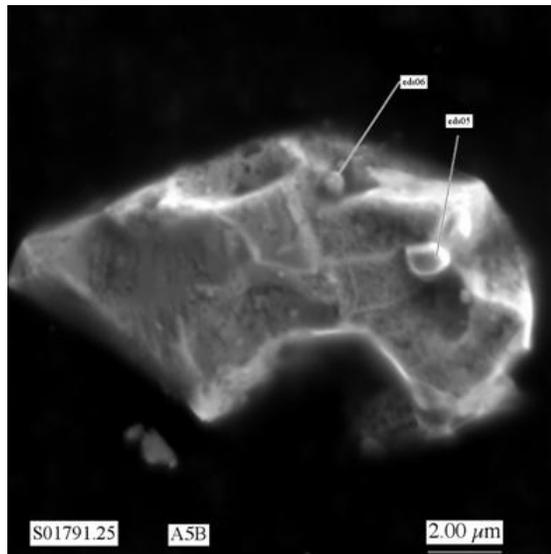


pH=3



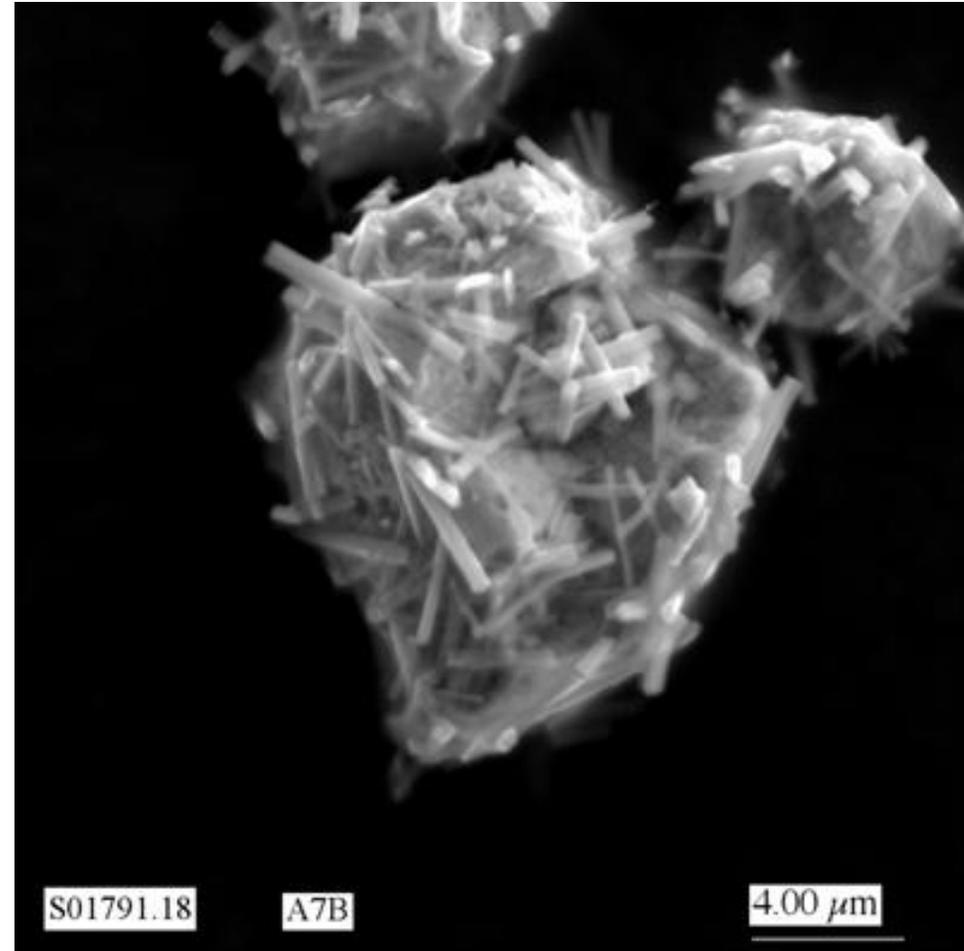
pH=4

pH=5

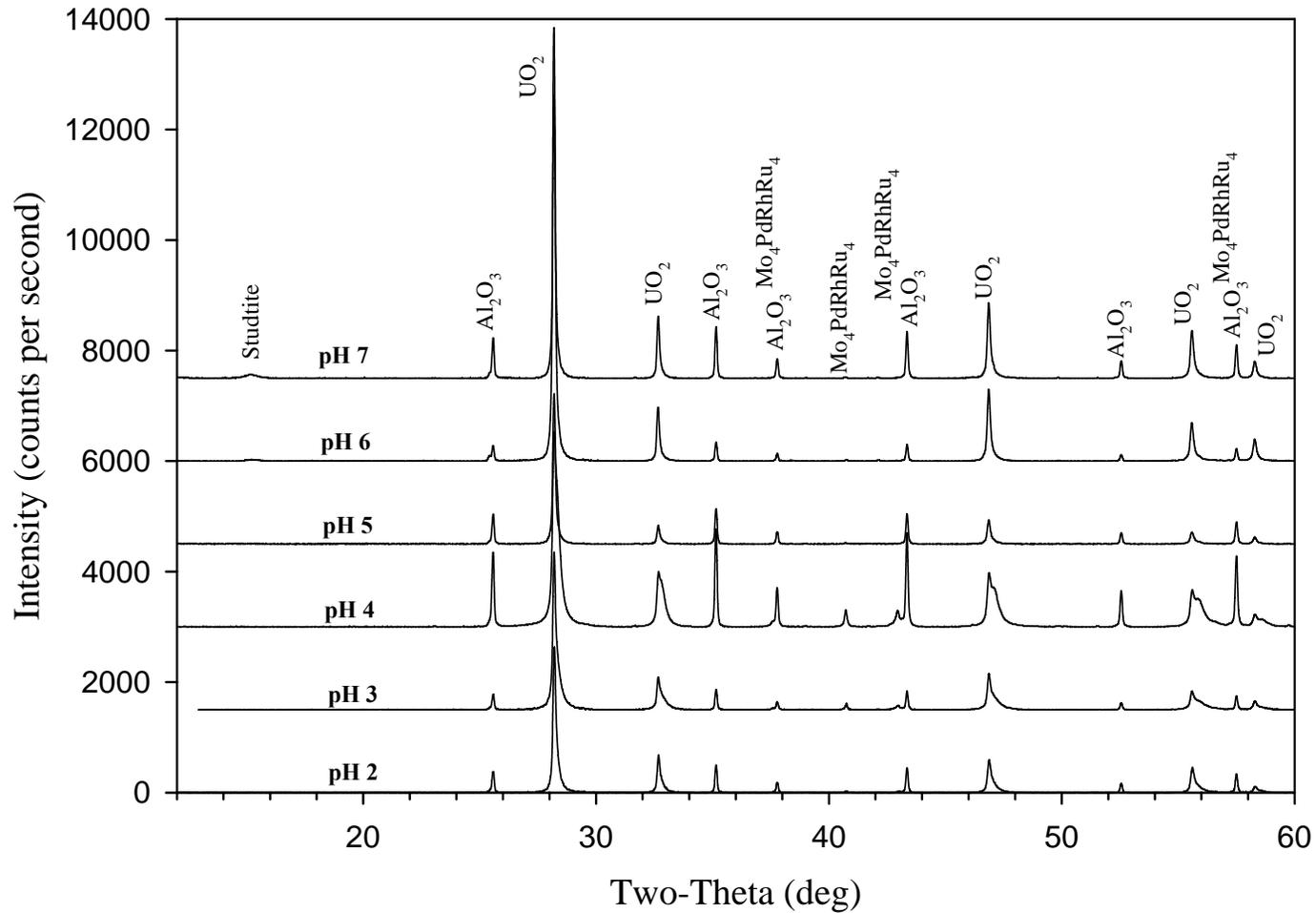


STUDTITE FORMATION

- Pump failure for about 2 days on pH 7 sample.
- Sample had 12.6% cumulative U release
- Pump restarted and test ran an additional 10 days (additional 1% reaction)
- XRD identified as studtite
- Is the radiolysis from the sample itself or background in hot cell?



XRD OF LOW pH SPFT SAMPLES



DISCUSSION OF LOW pH RESULTS

- Rates (both normalized to initial surface area and cumulative release) for pH 2, 3, and 4 show a decrease by factor of ~2 after ~30% and again after ~60% reaction.
- Below pH 5, some areas enriched in Zr, Pu, and Mo. (Note that cumulative release for pH 6 and 7 was ~14%, all others >25%)
- All samples show enrichment of ϵ -phases.
- Broad peaks on upper end of UO_2 peaks is fitted by U_4O_9 , but that phase is not expected to exist under these conditions. Possible Pu/Zr/Mo/U oxide phase.



FUEL CHEMISTRY SIMPLE MODEL

- **Using radiochemical data for U and Pu, and accounting only for Pu and Zr, about half of the necessary surface area reduction is modeled.**
 - **Total [Pu] and [Zr] in spent fuel is about 2 at%**
 - **Assume Zr released at same rate as Pu (1/6-1/3 that of U)**
 - **Pu⁺⁴ or Zr⁺⁴ affects 12-nearest neighbor U**
 - ◆ **Net negative charge delays oxidation (O⁻² transport and interstitial location)**
 - ◆ **Limits the ability of U to be in +5 or +6 state**
 - ◆ **Donor-acceptor site blocking**
 - ◆ **Less soluble and decreases surface area**



GRANDSTAFF THEORY

- Effect is both a surface area effect- if the dopant is less soluble or dissolves slower than the UO_2 , then it will build up on the surface and decrease the effective surface area until “excavated”- and a semiconductor effect – impurities alter ability for electron transfer
- Dopants can make UO_2 either more p-type or n-type
- U_3O_8 is n-type so dissolves fast.

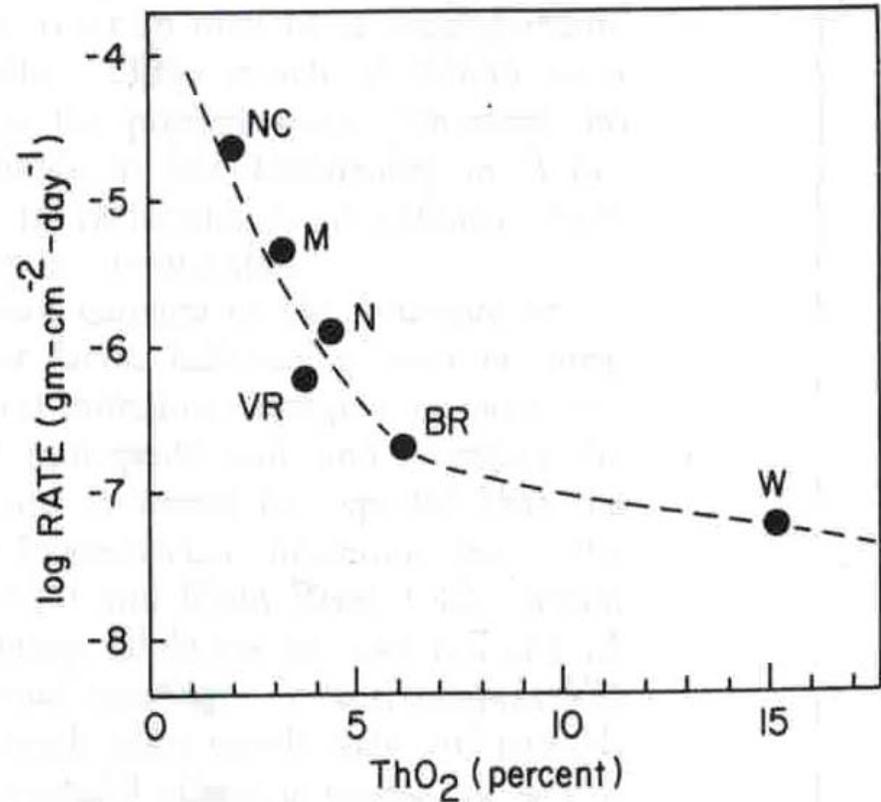


FIG. 4. Rate of uraninite dissolution as a function of uraninite ThO_2 content. ($T = 23^\circ\text{C}$, ambient air, distilled water.)

(Grandstaff, *Economic Geology*, 71(1976)8 pp1493-1506



CORROSION MECHANISM

- Habashi and Thurston developed a model for dissolution kinetics
 - A_1 =SA of cathodic zone
 - A_2 =SA of anodic zone
 - Assumption of constant surface area only valid for very small total reaction
- With fuel chemistry variations (change in oxygen potential) is it possible for A_2 to significantly decrease?
- Even at the microscopic level, this shows that the entire exposed surface area can not be undergoing anodic dissolution

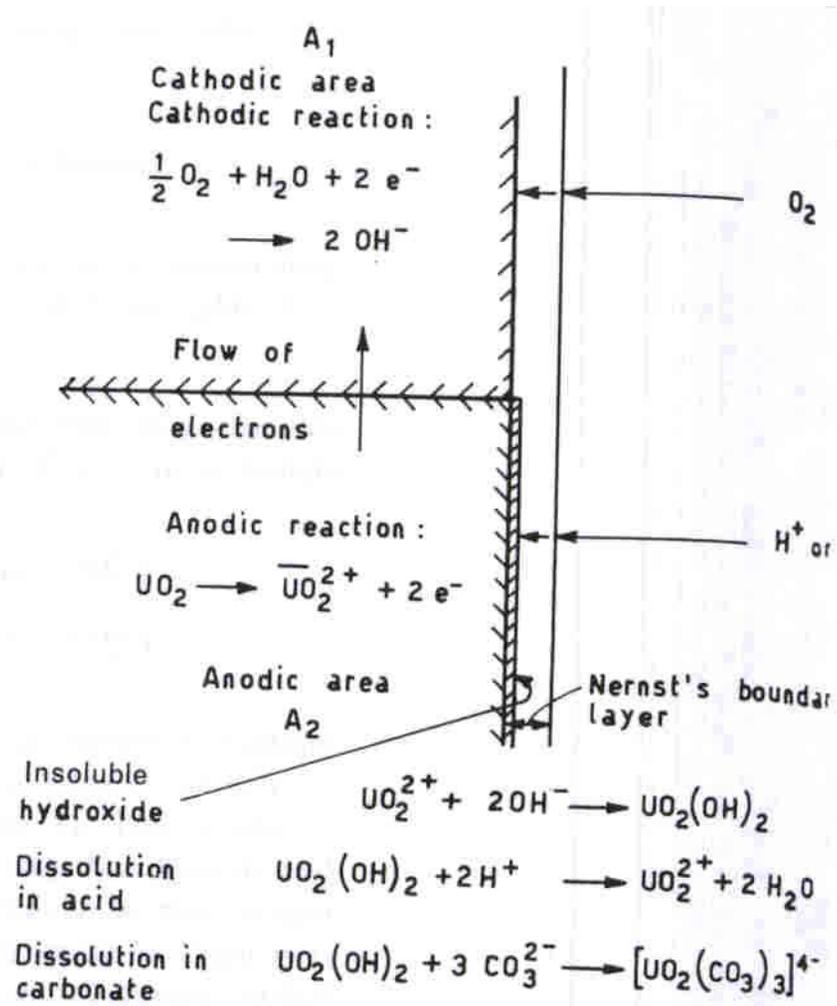


Fig. 4 - Schematic representation of the electrochemical reactions during the leaching of uranium dioxide.

(Habashi & Thurston, *energia nucleare*, vol 14, 4(1967)238-244)



DONOR/ACCEPTOR SITE EFFECTS

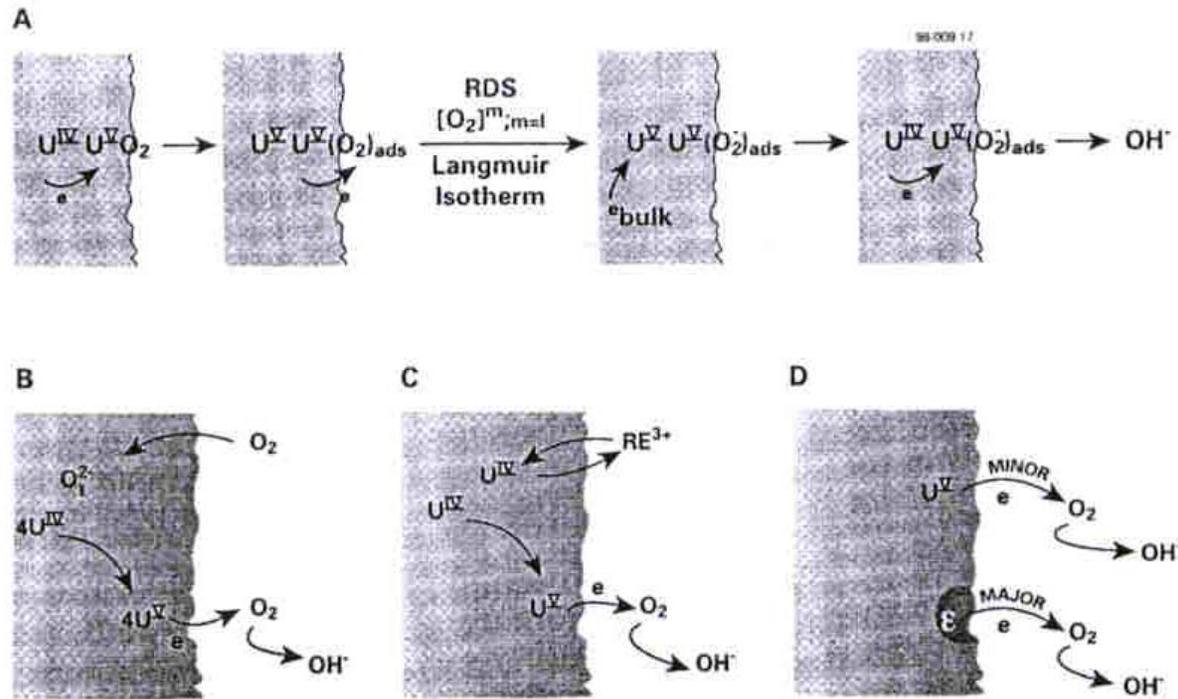


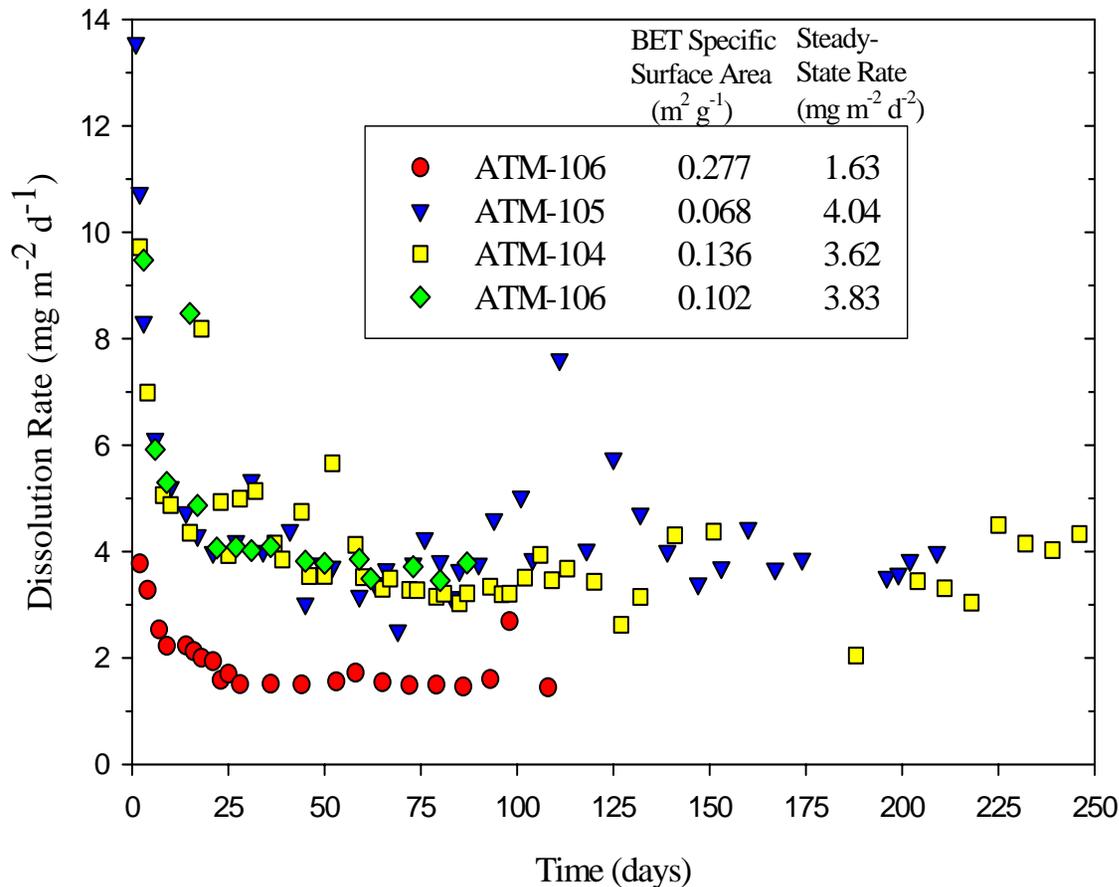
Fig. 19. Schematic diagrams illustrating the influence of various factors on a O_2 reduction on a UO_2 surface: (A) mechanism of reduction at donor-acceptor sites; (B) effect of corrosion on the number density of donor-acceptor sites; (C) effect of rare earth doping on the number density of donor-acceptor sites; (D) catalytic effect of noble metal particles (ϵ phase).

Fission products and actinides will alter the U(IV)/U(V) or U(V)/U(VI) relationship especially at higher burnups (after sufficient decay) and extended corrosion.

Shoosmith, JNM 282(2000)1-31.



NORMALIZED DISSOLUTION RATES



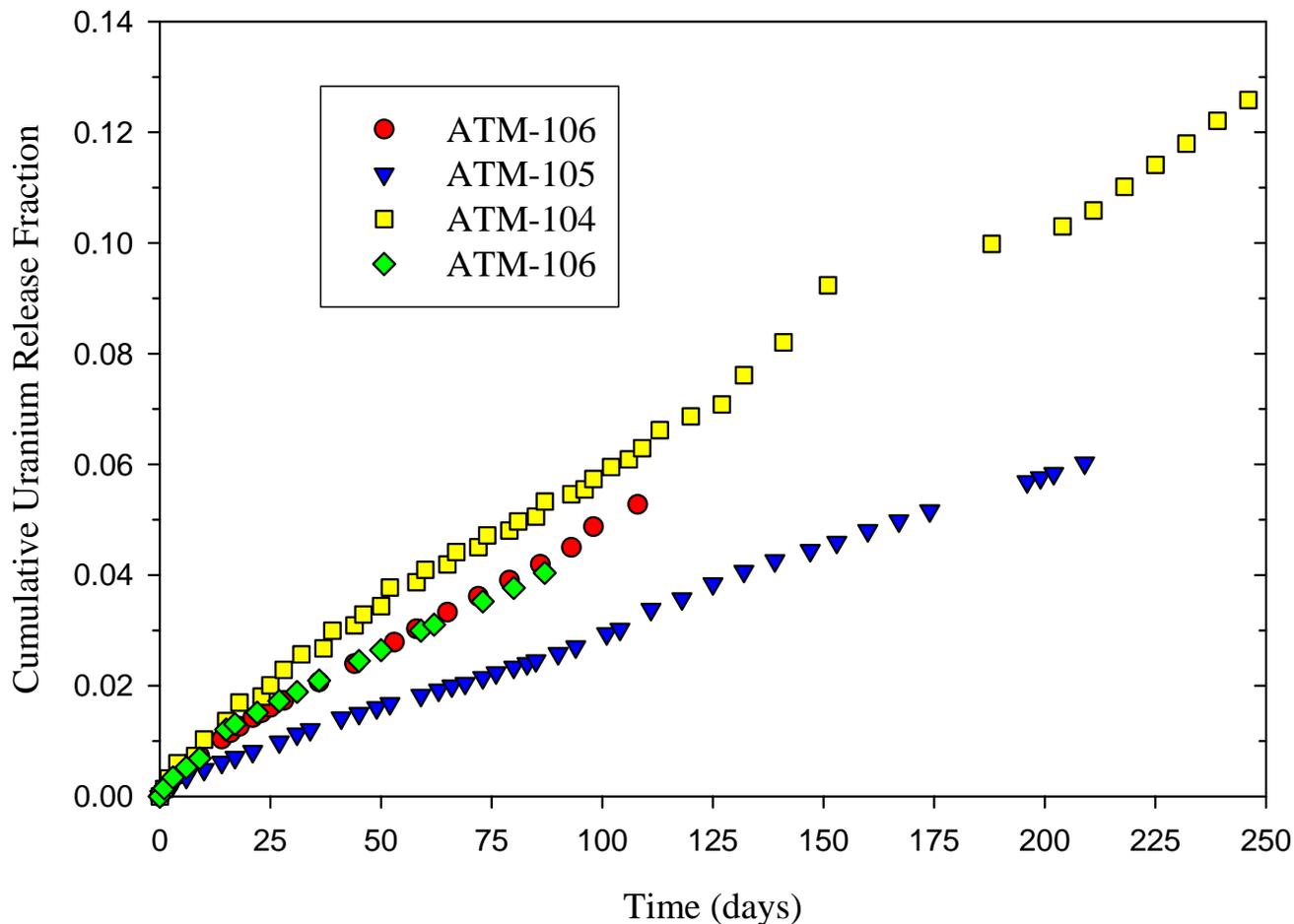
Hanson & Stout, MRS 2004

- The two ATM-106 samples differ in rate by the same factor as specific surface area, but changing SA changes rate in wrong direction.
- Appears ATM-105 (lowest burnup) has *fastest* rate, but is that just due to the very small specific surface area?
- No increase in rate even though normalized to a fixed initial surface area.

Dissolution rates of spent fuel in aerated water containing 2E-2 M carbonate/bicarbonate, pH=8, at 25°C



CUMULATIVE RELEASE



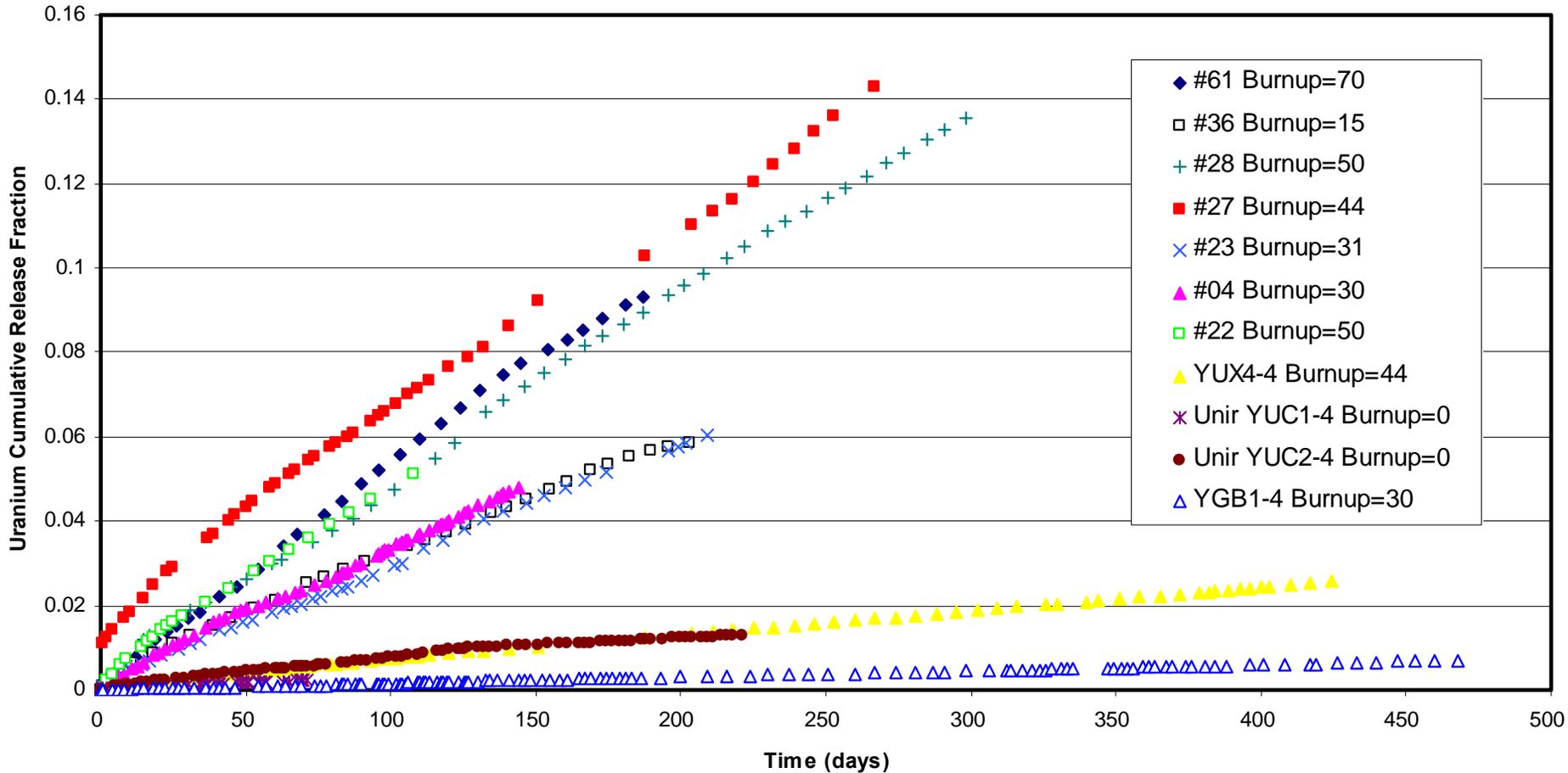
- The two ATM-106 samples now identical.
- ATM-104 same as 106 when corrected for early oxidation.
- Appears ATM-105 (lowest burnup) has *slowest* rate.
- No increase in rate over time.
- Smooths out fluctuations, but assumes constant parameters in-between data points.

Hanson & Stout, MRS 2004



SURFACE AREA AND RADIOLYSIS

Burnup Dependence- U Cumulative
T= 25 C, 2E-2 Carbonate, 0.2 Oxygen, pH=8



All samples are powders except for YUX4-4 and YGB1-4



S&T FUTURE WORK

- **Previous tests focused on the effects of water chemistry**
- **S&T focus is on**
 - **Fuel chemistry**
 - ◆ **Doped UO₂**
 - ◆ **RADFUEL**
 - **Radiolysis effects**
 - **Effective surface area**
 - **Dependence on water flux/contact mode**
 - **Effect of secondary phases on matrix corrosion**
 - **Eventually to perform spent fuel tests**
 - ◆ **Partitioning of Tc and other radionuclides**

